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Dr. A. K. Vasudevan, code 1222
Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217-5000

re: Contract #N00014-91-C-0067

Dear Dr. Vasudevan:

Please find attached one copy of the quarterly (September-November) technical report in accordance with the contract above.

Work during this last quarter has centered on PZT and its properties.

Yours sincerely

Dr. M.S. Duesbery
Vice-President
Fairfax Materials Research, Inc.

cc: ACO
NRL
DTIC (2)

Computer Modelling of Cyclic Deformation of High-Temperature Materials

TECHNICAL PROGRESS REPORT

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September 1, 1993 through November 30, 1993

I. Introduction and Program Objective

Current methods of lifetime assessment leave much to be desired. Typically, the expected life of a full-scale component exposed to a complex environment is based upon empirical interpretations of measurements performed on microscopic samples in controlled laboratory conditions. Extrapolation to the service component is accomplished by scaling laws which, if used at all, are empirical; little or no attention is paid to synergistic interactions between the different components of the real environment. With the increasingly hostile conditions which must be faced in modern aerospace applications, improvement in lifetime estimation is mandated by both cost and safety considerations.

This program aims at improving current methods of lifetime assessment by building in the characteristics of the micro-mechanisms known to be responsible for damage and failure. The broad approach entails the integration and, where necessary, augmentation of the micro-scale research results currently available in the literature into a macro-scale model with predictive capability.

In more detail, the program will develop a set of hierarchically structured models at different length scales, from atomic to macroscopic, at each level taking as parametric input the results of the model at the next smaller scale. In this way the known microscopic properties can be transported by systematic procedures to the unknown macro-scale region. It may not be possible to eliminate empiricism completely, because some of the quantities involved cannot yet be estimated to the required degree of precision. In this case the aim will be at least to eliminate functional empiricism. Restriction of empiricism to the choice of parameters to be input to known functional forms permits some confidence in extrapolation procedures and has the advantage that the models can readily be updated as better estimates of the parameters become available.

II. Program Organization

The program has been organized into specific tasks and subtasks as follows.

Task 100. Lifetimes of metallic dispersed-phase composites

Most service materials fall into the category of dispersion-hardened metallic composites. This task will consider the problem of dispersion hardened materials in general, but with two specific materials, NiAl and $MoSi_2$/SiC in mind.

Task 110. Identification and modelling of micromechanisms

The purpose of this task is to determine what micromechanisms are operative in the high-temperature deformation of dispersion-hardened materials. In the general case this will be done by a literature search. For specific materials, the micromechanisms will be determined from the

experimental program at NRL. Once identified, each of these micromechanisms will be modelled, in order to determine what are the critical parameters which determine its effect on plastic flow and values for these parameters. Also to be determined is whether the modelled critical values are dependent on quantities which must be obtained from a smaller scale model.

Task 111. Equiaxed dispersoids

This task will consider dispersions of the type encountered in NiAl-like materials. That is, the dispersoids are considered to be small compared to the grain size. The term 'equiaxed' is used because the particles are roughly of the same size in all three dimensions. However, this is not a requirement for this task. Rather, it is necessary that the particles not be too large in the dimension normal to the slip plane, so that they can be surmounted with relative ease by cross-slip and/or climb without the generation of appreciable back-stress.

Task 112. Anisotropic dispersoids

This task covers the case of dispersoids which are elongated in the direction normal to the slip plane. An example is SiC fibers in $MoSi_2$. In this case, plastic flow around the dispersoids takes place by a combination of glide and climb, but is a protracted process during which large stresses acting in opposition to the applied load are developed.

Task 113. Grain boundary effects

This task will examine the role of grain boundary processes in high-temperature deformation.

Task 120. Macroscopic stochastic model for creep

In real materials it is likely that more than one mechanism will be operative, either in parallel or in series. The information gained in task 110 is not sufficient to describe this situation. Once the critical parameters for individual mechanisms have been determined, it is necessary to combine them in a macroscale stochastic model. This will be done by determining critical stresses and activation enthalpies as a function of local geometry and using these values in a finite-temperature simulation of creep through a random array of dispersoids. Careful attention must be paid to possible interactions between mechanisms.

Task 130. Extension to cyclic deformation

The final step in task 100 is to extend the results to the case of cyclic deformation. Irreversibility is an intrinsic feature of the model in task 120. However, it is likely that other, as yet unrecognized, characteristics of cycled deformation will have to be considered.

Task 200. Lifetimes of piezoelectric ferroelectrics

Failure in cyclic loading of sensors and actuators formed from lead zirconate titanate (PZT) is a continuing problem. PZT is a ceramic and therefore differs from the materials considered in task 100 in that plastic deformation is not involved. This task will examine, modelling as necessary, the operation of PZT devices, in order to determine the factors governing lifetime limitation.

Task 300. Reporting

Running concurrently with tasks 100 and 200, this task will inform the Navy Program Manager and Contracting Officer of the technical and fiscal status of the program through R&D status reports.

III. Technical Progress

Task 100. Lifetimes of metallic dispersed-phase composites
Task 110. Identification and modelling of micromechanisms

One publication of relevance to the present program is appended to this report.

"On the Theory of Normal Grain Growth" by Louat and Duesbery, contains some new thoughts on the problem of grain growth.

Task 200. Lifetimes of piezoelectric ferroelectrics

The utility of PZT as a 'smart material' is severely limited by its premature mechanical failure when subjected to cyclic loading. The cause of this failure forms the critical question. The central problem is that an irreversible mechanism is necessary to explain the experimental observations, while the overt physical properties - that is, piezoelectricity, ferroelectricity and ferroelasticity - are all symmetric to reversal. A theory will be presented which introduces an intrinsic irreversibility and, at the same time, explains all salient experimental observations. Critical experiments and modelling directions will be detailed.

The key experimental observations are as follows.

⋆In the poled state, ferroelectric domains are elongated strongly in the direction of the poling field and are separated by walls with little curvature.

⋆Under cyclic mechanical loading at 70% of the monotonic fracture stress, the lifetime is in excess of 10^7 cycles. At stress amplitudes from 75% to 95% of the fracture stress, the lifetime decreases sharply from 10^5 to 10^2 cycles)[6]. The effect of temperature is unknown.

⋆Under cyclic (resonant) electrical loading, the lifetime depends on temperature. For deformation above 80° C, failure is much more rapid than below this critical temperature. Predeformation below 80° C prior to high-temperature deformation leads to even more rapid failure. Damage is not detectable for deformation below 80° C, but is observed as intergranular cracking at higher temperatures[6].

a. Theory

a.1 Fracture at Grain Boundaries

Work in previous reports has shown that when the c/a ratio is high, it is energetically favorable for the misfit to be concentrated into dislocations rather than distributed as coherent elastic strain. The formation of dislocations requires that they be drawn in from grain boundaries, and there remain the questions of whether this is mechanically possible and whether the resul;tung stresses can lead to micro-cracking at the boundary.

Many, if not all, domain walls terminate at grain boundaries. Among those that do, some are in a state of tension directed in a direction which is more or less normal to the boundary. The magnitude of the stresses are readily calculated on the basis that the transformation strain is accommodated coherently at domain walls. These strains may be represented as a uniform continuum of elementary dislocations. For a pair of domain walls specified as passing through the points $x = \pm a$ and as terminating at $y = 0$ and $y = L$ the normal stress at a point x,0 is given by

$$\sigma_{yy} = \frac{\mu\eta}{2\pi(1-\nu)}\int_0^L \left[\frac{(a-x)(3y^2+(a-x)^2)}{((a-x)^2+y^2)^2} + \frac{(a+x)(3y^2+(a+x)^2)}{((a+x)^2+y^2)^2}\right]dy \qquad (1)$$

$$= \frac{\mu\eta}{(1-\nu)}$$

This stress is expressed in terms of the shear modulus rather than of Youngs modulus, because the configuration considered is one of plane strain. Since σ_{yy} is technically large, of the order of a few percent of the shear modulus, local fracture of the grain boundary is then a possibility. A prerequisite for such fracture is the presence of embryonic cracks. These may occur by chance but their certain presence cannot be assumed. Rather, we note that the shear stresses which are developed at the ends of a domain in tension are of such a nature as to allow the possibility of the spontaneous generation of a lattice dislocation dipole with separation equal to the width of the domain. It will be shown that this configuration can act as a crack nucleus. To achieve this change in configuration it is necessary that elements of displacement on each wall, which are initially spread uniformly, glide so as to accumulate as a single dislocation. It may be seen that this process would result in the appearance of a dislocation dipole pair, with separation equal to the width of the domain.

A first task in the quantification of this process is the determination of the conditions necessary for it to occur. In general, a mechanism can be ongoing only if it satisfies conditions relating to both kinematics and energetics. Here, satisfaction of kinematics is embodied in the assumption that elementary dislocations can glide along the domain wall. To satisfy requirements on energy we have only to show that it decreases monotonically during this process.

To do so it is necessary to perform two integrals. The first gives the increase in energy resulting from the agglomeration of elementary dislocation; the other represents the decrease in energy which arises from the action of shear stresses in enforcing this motion. The result of the first calculation is well known; the increase in energy is simply:

$$\frac{\mu b^2 \ln \frac{S}{r}}{4\pi(1-\nu)}. \tag{2}$$

Here, μ is the shear modulus, ν is Poissons ratio, b is the resultant Burgers vector, S the distance over which the strain has been agglomerated and r the dislocation core radius. Clearly, $b = S\eta$, where η is the misfit parameter. Since there one dislocation is involved on each domain wall, (2) represents one half of the total energy involved.

Next consider the work done by the shear stresses. The stresses are readily evaluated by again representing the elastic misfit across a domain wall as a dislocation continuum so that the shear stress at a point with coordinates x,y, referred and due to an element of dislocation of amount $\eta \delta x$ is:

$$\frac{\mu \ \eta \ \delta x \ x(x^2-y^2)}{(x^2+y^2)^2}. \tag{3}$$

Using this stress, together with that due to a similar element from the other wall, one finds by integration that the shear stress at a point with coordinates (0,y) referred to an end of a domain wall is (when, as is to be expected here, $y/L << 1$)

$$\frac{\mu \eta \ln(2\frac{a}{r})}{2\pi(1-\nu)}. \tag{4}$$

From this it is found, again by integration, that the work done in formation of a dipole, of width 2a, is

$$\frac{\mu b^2 \ln(2\frac{a}{r})}{2\pi(1-\nu)}. \tag{5}$$

The process will be ongoing provided

$$2a \geq S = \frac{b}{\eta}. \tag{6}$$

It remains to examine the response of the grain boundary lying between the elements of the dipole to the combined stresses present. To do so we calculate the force which acts to cause the juncture of a pair of symmetrically disposed cracks which terminate at the positions of the dipole elements. Specifically, taking $x=0$ to represent the mid-point of the length, 2a, of boundary in question, we suppose the cracks to lie in the ranges: $-a \le x \le -c$; $c \le x \le a$. Further, we suppose that a dislocation dipole-pair of appropriate sense having Burgers vectors of magnitude b lie at the points $x \pm a$.

To evaluate the crack extension force it is necessary to determine the dislocation distribution function, f(x) and then use the result given by Bilby and Eshelby for the crack extension force, G, which operates at the points $x = c$. That is

$$G = Lim\ (x \to c)\ \frac{\pi^2 A\lambda(x-c)f^2(x)]}{2} \tag{7}$$

where λ represents the magnitude of a unit dislocation and

$$A = \frac{\mu\lambda}{2\pi(1-\nu)}. \tag{8}$$

The distribution f(x) is given by

$$f(x) = \frac{1}{\pi^2 A(1-\nu)\sqrt{(a^2-x^2)(x^2-c^2)}}\int_D \frac{\sqrt{(a^2-t^2)(t^2-c^2)}\,\sigma(t)dt}{(t-x)} + \frac{Q}{\sqrt{(a^2-x^2)(x^2-c^2)}}. \tag{9}$$

Integration in (9) is over the whole range, D, where dislocation occurs. $\sigma(t) = \mu/(1-\nu)$ and Q is such that the total amount of dislocation in the individual regions is b and -b. Performing the necessary integral

$$Q = \frac{a\ b}{K\left(\frac{\sqrt{(a^2-b^2)}}{a}\right)}, \tag{11}$$

where K (k) is a complete elliptic integral of the first kind. Integrating again

$$f(x) = \left(\frac{\mu\,\eta}{\pi A(1-\nu)^2}(a^2+c^2-2x^2)+\frac{a\,b}{K(k)\lambda}\right)\left(\frac{1}{\sqrt{(a^2-x^2)(x^2-c^2)}}\right). \qquad (12)$$

Substituting in (7)

$$G = \frac{\pi\,\mu}{4(1-\nu)c(a^2-c^2)}\left[\frac{2\eta^2)(a^2-c^2)^2}{(1-\nu)^3} + \frac{a^2b^2}{2K(k)^2} + \frac{2\eta(a^2-c^2)a\,b}{K(k)(1-\nu)}\right] \qquad (13)$$

For fracture this force must exceed the resistance due to the implied production of new surface. This is of amount $2\gamma_b$, where γ_b is the grain boundary surface energy density. This energy density is thought to be about one half of that of a free surface in the same material. Following Stroh this then about $\mu b/28$.

From the form of (13) it is apparent that G passes through a minimum at some value of c lying between 0 and a. Fracture can only occur if G at this minimum value exceeds a critical value of about $2\gamma_b$. The determination of the position and hence the magnitude of this minimum involves the solution of a quintic equation. The result will be given in the next report.

b. Plans

⋆ Continued modelling of the mechanisms of ferroelastic domain wall motion will be performed, with the aim of determining critical parameters which can be derived from or compared with experiment. Specific questions to be answered are:

1. Is the wall motion governed by the two-dimensional analog of kink pair nucleation and propagation, or by diffusive dragging of wall defects and dislocations?

2. How are these mechanisms influenced by an electric field of sufficient magnitude to stabilize the poled state?

3. How do the lifetimes of poled and unpoled specimens compare?

⋆ Domain wall motion in the coherent strain limit will be examined.

Phil. Mag., in the press

On the Theory of Normal Grain Growth

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Abstract

The theory of normal grain growth that invokes random walk is further extended by allowing for biases in step direction. It is concluded that the predictions of this theory are in overall quantitative accord with experiment. However, a conclusion as to the degree of agreement between theory and experiment as to the exact form of the grain size distribution function remains in doubt because of a lack of precision in the definition and measurement of grain size. Possibly, this difficulty may be surmounted by replacing measurements of grain size by those of the lengths of grain boundary edges as found in planar sections of polycrystals.

Introduction

The first formulation of a detailed theory of normal grain growth was that of Hillert [1965]. Hillert [loc.cit] followed von

Neumann [1952] who recognised that the force for growth of an isolated n sided grain is

$$P = k(n-6),$$

where k is a constant. Hillert [loc. cit.] combined this conclusion with the experimentally observed proportionality between the size of a grain [Feltham, 1957] and the number of its sides and with the expectation that

$$\frac{d\lambda}{dt} \propto \frac{1}{t}.$$

to conclude that the rate of grain growth should be given by

$$v = \frac{d\lambda}{dt} \propto \left(\frac{1}{\lambda_1} - \frac{1}{\lambda}\right),$$

where λ_1 is the mean grain diameter.

From this juncture the mathematical analysis employed to derive the grain size distribution function follows that used by Lifshitz and Slyozov [1961] in dealing with the problem of Ostwald ripening. In this analysis an infinite dilution of the growing particles is assumed with the consequence that the effects of any direct interactions between individuals can be ignored. In using this approach to deal with normal grain growth Hillert was therefore supposing that the changes in sizes of individual grains were independent of the characteristics of their neighbours. But clearly the motions of neighbouring grains are in fact close coupled. Thus, for the two dimensional case it can be seen that the gain, for example, of a side by one grain can be accomplished only by the loss of a side of an associated

neighbouring grain. Similar conclusions hold in the case of three dimensions. We conclude that the analogy with Ostwald ripening is too remote to allow an unqualified adoption of the Lifshitz-Slyozov analysis.

A second approach stems from the work of Feltham [1957]. Feltham concluded that the observed distribution [Feltham, loc. cit., Beck, 1954] in both the number (n) of sides per grain and in grain size, was quite well represented by lognormal functions and sought to deduce the drift velocity from these facts. He was able to show that this distribution was compatible with a parabolic rate of growth in grain size, (λ). However, this analysis is not exclusive since it is equally applicable to any distribution that exhibits self-similarity.

Kurtz and Carpay [1980] noted further, that an approximate lognormality in size distribution could be ascribed to every class of grains characterized by a certain fixed number of sides. They also indicated that the distribution over all classes should then be expected to be lognormal and attempted to give a theoretical justification for such characterizations. The basis of their argument is a result of Kapteyn [1916] which may be paraphrased as: the motion of a random walker will lead to a lognormal distribution if its steps are variable and proportional to the local magnitude of the random variable involved. However, as can be shown [Louat et al., 1992] such proportionality obtains in respect to the number of sides to a grain but not to grain size.

The next attempt at an analysis leading to a distribution function for grain size was that of Louat [1974] who took the view that the processes of change in grain size are, to a significant extent, random in sign. His prime justification was that, the experimentally observed relation:

$$\lambda = k\ (n-6)$$

between grain size and the diameter of sides of grain edges is only statistically valid. Specifically, the diameters of grains having n sides obey a frequency distribution approximating to a lognormal [Feltham, loc.cit.]. A direct consequence is that it is generally not possible to specify the direction of growth of a particular grain of a given size. To illustrate, there is a significant probability that a grain having a diameter 1.1 times the mean has say, four sides rather than say, seven. Louat [loc.cit] thought that this feature should be important in the mechanism of grain growth. Since it was unclear how Hillert's approach should be modified to allow for this view, Louat [loc. cit.] simply ignored Hillert's approach, supposed that the probabilities that a grain experiences positive and negative increments in diameter were equal and aimed to judge the validity of these suppositions by comparing the results of the analysis based thereon with those from experiment. The grain size distribution function ,F, deduced on this basis is given by the appropriate solution to the equation:

$$\frac{\partial F}{\partial t} = A\frac{\partial^2 F}{\partial \lambda^2} \qquad (1)$$

The factor A is the rate parameter for the thermally activated process of grain growth. Surprisingly, the accord between theory and the most detailed experimental data, then available, that of Hu [1974] was excellent.

The relation predicted was

$$F(\lambda) = \lambda \{\exp(-\lambda^2 / A\,\lambda_1)\} / \lambda_1^{3/2}. \qquad (2)$$

Pande [1987] has recently attempted to combine directly, the essentials of the individual approaches of Hillert and Louat. He added the term involving the second spatial derivative of (1) to Hillert's [loc.cit.] conservation equation to obtain:

$$A_0\frac{\partial^2 F}{\partial \lambda^2} - B_0\frac{\partial (Fv)}{\partial \lambda} = \frac{\partial F}{\partial t} \qquad (3)$$

and found its solution with adjustable weighting for the two contributions through variation in the ratio of the constants, A_0 and B_0. This approach is not easy to justify since it requires the acceptance of the applicability of the Lifshitz-Slyozov approach. We shall return to the resolution of this question later. We shall argue that the natural way to combine the effects involved in Hillert's and Louat's outlooks is to modify that of Louat so as to allow the probabilities of grain increase and decrease to be a function of the grain size. We shall find, that the analysis leads to an equation which accords in form with that of Pande [loc. cit.].

We now review the bases and initial development of the theory of normal grain growth based on the concept of random walk in grain size space.

Theory of Random Walk in Normal Grain Growth

As originally suggested (Louat, loc.cit). The probabilities of growth and shrinkage in grain size were assumed be the same. On this basis the analysis is as follows. For a total population of N grains, the number which have linear dimensions lying in the range

$$\lambda - \frac{\delta\lambda}{2} \leq \lambda \leq \lambda + \frac{\delta\lambda}{2}$$

is

$$N\ F(\lambda)\ \delta\lambda.$$

Any change in this number must result from interchanges with adjoining populations. We assume that the fluxes are simply proportional to the population densities from which they originate. Thus, the net flux into an interval of length $\delta\lambda$, at λ is proportional to:

$$F(\lambda + \delta\lambda) + F(\lambda - \delta\lambda) - 2\ F(\lambda).$$

It follows from a Taylor expansion of $F(\lambda,t)$ that the time rate of change of F is:

$$\frac{\partial F}{\partial t} = B\ \delta\lambda^2 \frac{\partial^2 F}{\delta\lambda^2} \qquad (4)$$

where B is a rate determining constant. This equation is analogous with the well-known diffusion equation in which the quantity,

$$S = B\delta\lambda^2, \qquad (5)$$

becomes, $D = \nu a^2$, the diffusion coefficient. Here, a is a constant which is related to the lattice parameter and ν is the frequency with which a diffusing atom jumps the distance, a. This distance is clearly a constant. In the case of grain growth the situation is more complicated and it is necessary to examine the quantity, S in detail. To this end we consider the behaviour of a particular face of an arbitrarily chosen grain. In general this face will, under the action of forces generated from surface energy, be moving towards an elusive position of equilibrium. Elusive, because this position changes more or less discontinuously with time as some grain faces in the neighbourhood change association from one grain to another and some vanish altogether. The resultant motion of the specified face will be irregular in both rate and direction. However, it is to be expected that the amplitude of these movements and the accompanying changes ($\delta\lambda$) in grain size will vary linearly with the scale of the system; that is with mean grain size, λ_1. Compatibly, we conclude that,

$$\delta\lambda = \alpha\lambda_1. \qquad (6)$$

where α is a numerical constant. Again, as previously stated, and as is generally accepted, the self-generated pressures, p, which engender boundary motion scale inversely with mean face diameter, and so with mean grain size. Thus, the speed of a face varies as,

$$v = Mp = \gamma M/\lambda_1$$

where M is the grain boundary mobility and γ is a constant. Consequently the time to effect the change $\delta\lambda$ will vary as,

$$\delta t = \alpha\delta\frac{\lambda}{v} = \frac{\alpha^2\lambda_0^2}{\beta M} \qquad (7)$$

Now, the quantity B in (4) is clearly the rate at which jumps of size $\delta\lambda$ are made and so

$$B \propto 1/\delta t$$

and from (6) and (7),

$$B\ \delta\lambda^2 = \gamma.$$

This quantity is proportional to the grain boundary energy density.

We now find a suitable solution of (4), which has become

$$\frac{\partial F}{\partial t} = \gamma\frac{\partial^2 F}{\partial\lambda^2}. \qquad (8)$$

To satisfy the constraint that grains are destroyed but not created, we adopt the boundary condition $F(\lambda) = o$, when $\lambda = 0$. The required solution is then found to be:

$$F(\lambda, t) = \frac{C\,\lambda\, e^{-\lambda^2/4\gamma t}}{\gamma t^{3/2}}, \qquad (9)$$

where C is a disposable constant.

This then, is the theory as originally proposed. As stated above it is unsatisfactory in that the probabilities of growth and shrinkage are taken to be the same. We now attempt to rectify this matter. As originally suggested the processes of normal grain growth were seen to have a random component that arises because grain boundary motion leads to intergranular collisions in which faces are gained and lost in a somewhat random manner. The

probabilities of the resultant growth and shrinkage in grain size were assumed to be the same. We shall now examine these probabilities and find that they vary with grain size. As a first step in this process we consider the change in configuration illustrated in fig.1.

Fig. 1. Interchange of grain sides

Here, the merger of the corners X and Y and their replacement by S and T, is accompanied by the loss of one side by each of the grains A and B and a similar gain by C and D. The converse is true if S and T merge. Thus, a grain, A, for example, may either gain or lose a side through such an event. A crucial question is: to what extent is the choice between these alternatives determined by the characteristics of grain A alone? Towards an answer we first refer to the grain corner illustrated in fig. 2.

Figure 2. Geometry at Grain Corners

Here the lines, OX ,OY, Oz represent a trio of grain edges which meet at a point. We consider first, cases where the number of sides to the grain considered, A, exceeds six, so that the mean value of α (see fig.2) is greater than $\pi/6$. We see, as shown, that the point O is not at a position of equilibrium and that it will tend to move in response to forces directed along the directions ,OX, etc. Depending on whether the direction of the resultant (OS) of these forces lies within or without the right angle YOR, the grain edge, OY, will respectively shorten or lengthen. Resolving forces, the condition for changes in OX and OY to have opposite signs (unpaired changes) is easily shown to be:

$$\cos(\phi+\alpha) < 2\cos^2\alpha. \qquad (10)$$

When $n > 6$ this condition is satisfied unless ϕ may be regarded as small. Thus, when $n = 7$, $\alpha = 64.29°$ we find that, on average, changes are unpaired unless $\phi < \phi_c$, $\phi_c = 3.62°$. When changes are paired both sides lengthen, as von Neumann's result might be thought to indicate. The most restrictive case occurs when $\phi = \phi_{max}$, the grain is twelve sided and $\phi_{max} = 7.5°$. For $n < 6$, we find, for all n, that the motion is paired and such as to shorten both OX and OY.

Consider further, the case of a grain for which $n > 6$. On average grains of this class are surrounded by other grains that have fewer than six sides and so tend to shrink or more

specifically, to lose sides. Thus, if in a particular grain, the average angle between adjoining sides is, $2\pi(1/2-1/n)$, then the external angles at these corners will average:

$$\pi(1/2 + 1/n). \qquad (11)$$

It follows from (11) that, on average, the external grains will have a tendency to lose sides held in common with the internal grain. Furthermore, since the number of sides to a grain is necessarily integer, this tendency is concentrated in one or more particular grains. Thus, we have two countervailing influences on a side held in common. From the internal grain there is a tendency to gain sides. From the external grains there is a tendency to lose sides. The difference between the current value of (11) and that when $n = 6$ is a measure of the nett bias. Substitution of appropriate values for n shows that the biases indicated by (11) and by the value of ϕ, see (10) are comparable. Thus, we are led to the view that, for $n > 6$, the probabilities of gaining and losing sides, are nearly the same. We conclude, then, that for n in this range, the processes by which grains gain and lose sides are in the main random rather than directed.

The situation is different when $n < 6$ because (10) is satisfied for all ϕ, when α takes its mean value, which is less than $\pi/3$. Thus, (10) can fail and the grain have a tendency to gain a side only at those corners at which stochastic variation provides a value of α exceeding $\pi/3$. Such excursions can be expected to be reasonably common when $n = 5$ and $\alpha = 54°$, but rare, when $n \leq 4$; $\alpha \leq \pi/4$.

We conclude that grains with six or more sides will show little correlation between their size and rate of growth. On the other hand, such a correlation should become increasingly apparent for decreasing, n, in the range: $n < 6$. These conclusions seem to be in complete accord with the results of computer simulations [Srolovitz et al.,1984]. Specifically, it is found that the mean rate of growth of grains in the range $n \geq 6$ is that of the mean rate of all grains, but that individual grains of this class follow random growth paths. These involve frequent changes in direction of growth: sometimes growing sometimes shrinking. In the case of grains for which $n \leq 5$ the mean growth rate of each number class is, with decreasing n, progressively smaller than that of the mean.

The acceptance of these results requires a modification of the analysis leading to (2). We consider the fluxes of grains in and out of a particular interval of grain size. To represent differing probabilities of growth and shrinkage we introduce a function, $g(\lambda)$ such that the flux of grains from size, λ to size $\lambda + \delta\lambda$ is proportional to:

$$f(\lambda) \{ 1/2 + g(\lambda) - g(\lambda + \delta\lambda) \}.$$

From a Taylor expansion of $f(\lambda,t)$ we find a relation:

$$\frac{\partial f}{\partial t} = B\delta\lambda^2 \left(c\frac{\partial^2 f}{\partial \lambda^2} - d\,\frac{\partial f \partial g}{\partial \lambda^2} + d\,f\,\frac{\partial^2 g}{\partial \lambda^2}\right)$$

where c and d are constants. This equation, is analogous to the relation representing diffusion in the presence of a potential gradient, $-\partial g/\partial\lambda$. It may be noted that when

$$v = \frac{\partial g}{\partial \lambda}$$

it accords in its essentials with that of Pande (loc. cit.)and that, as he has shown, the adoption of this form can result in a modification of the shape of the distribution function such as to vary the agreement between theory and experiment.

Experimental data are generally obtained from measurements on two dimensional sections of three dimensional agglomerates. It is therefore of interest to investigate the implications of this fact. We note that the discussion which leads to (1) and (4) is non-dimensional and in fact is as applicable to grain growth in three dimensions as it is in two. Accordingly ,the distributions in two and three dimensions should be the same. Using the simple approximation that the grains are spherical it is easily shown [Louat, loc.cit.] that the transformation giving the two dimensional distribution (f(x)) in terms of that for three (F(λ)) is

$$\frac{F(x)}{x} = 2\rho \int_x^\infty \frac{f(\lambda)}{(\lambda^2 - x^2)^{1/2}} d\lambda,$$

where ρ is the number of grains per unit volume. Substitution for f(λ) from (2) shows that, as required, F and f differ only by a numerical factor.

The integration of a distribution function over its range a of applicability gives the total population. On this basis we find from (9) that

$$N(t) = c\ t^{-1/2}.$$

This result implies, the usually quoted, grain growth rate of, $t^{1/2}$. Other growth laws may be seen to follow if we suppose that

$$v = M\, p^n$$

where $m = n + 1 \geq 1$, in which case, proceeding as before,

$$B\ \delta\lambda^2 = \eta\lambda_1^n.$$

In these circumstances (1) becomes:

$$\frac{1}{\lambda_0^n}\frac{\partial f}{\partial t} = \frac{\partial^2 f}{\partial \lambda^2} = \frac{\partial f}{\partial \tau} \qquad (12)$$

where λ_1 is the mean grain size:

$$\lambda_1 = (\pi\beta\tau)^{1/2}$$

of the distribution:

$$F(\lambda,\tau)) = \frac{C\lambda e^{-\lambda^2/4\beta\tau}}{\beta\tau^{3/2}} \qquad (13)$$

where

$$\tau = \int \lambda_0^n dt = \int (\pi A\tau)^{n/2} dt.$$

Thence, we have a grain size time dependence specified by:

$$(\pi\beta\tau)^{1/2} = t^{1/(2+n)}.$$

Thus, for the usually quoted case of boundaries exhibiting Newtonian viscosity ($n = 0$, $m = 1$), we recover the standard result. For $n = 1$ ($m = 2$), we find the commonly observed, $t^{1/3}$ dependence.

It is a non-trivial characteristic of (9) that the

distribution of grain sizes is independent of the parameter, n. Importantly, this prediction has been confirmed by experiment (Hu, loc. cit.).

We now pass to a consideration of grain shape; specifically to the distribution of the number of faces , or in two dimensions, of edges per grain. Clearly the experimental data, which relate to two dimensions, are represented by a lognormal function. All authors, including Hu [loc. cit.], who found that his grain size distribution was not well approximated by a lognormal, appear to agree on this point. It would appear that the distributions of size and shape are different. Allowing that there is a difference no prediction seems to have yet been advanced as to the shape of this distribution.

Towards such prediction we suppose, consistent with ideas expressed here and previously [Louat, loc. cit.], that the gain and loss of grain sides by an individual grain is a random process. Accordingly, we suppose that the nett change δN in a time t in a population of N sides, to be proportional to N ($\delta N/N \ll 1$). If then, we choose N such that

$$N = rn,$$

that is, if we select a sample consisting of r grains, with each initially having n sides, we see that the change in the average number of sides associated with nett change δN is, for r necessarily constant:

$$\delta n = an,$$

where a is a constant.

Now, distributions developed through random processes in which the step size, δx is a function of a random variable x, i.e. $\delta x = k(x)$, have been studied by Kapteyn [1916]. Here, we are concerned with the case where $\delta x \propto x$. For this case Kapteyn shows that the resulting distribution is lognormal:

$$\Phi(n) = \frac{e^{-\frac{(\ln n/n_0)^2}{2\sigma^2}}}{(2\pi)^{1/2}\sigma n}. \qquad (14)$$

It remains to determine the magnitude of the constants σ and n_0. We can do so by imposing the topological and experimental constraints [Smith, 1952] that the average grain must have 6 sides and that the most common has 5.

To satisfy the first requirement we write

$$6 = \int_{-\infty}^{\infty} n\, e^{\frac{-\ln^2(\frac{n}{n_0})}{2\sigma^2}} \frac{dn}{n} = n_0 e^{\frac{\sigma^2}{2}}.$$

To satisfy the second condition we require that the maximum of the distribution occurs at n = 5. This gives the relation

$$n = n_0 e^{-\frac{\sigma^2}{2}}.$$

Combining these two equations we find that

$$\sigma = 0.32$$

and that

$$n_0 = 5.7.$$

These then, are the essential bases of the theory. However, it is to be noted that grains as such, have little physical significance: They are merely the topologically simplest description of closed boundary surfaces in polycrystals.

Furthermore, it is the faces rather than the grains themselves, which play a direct role in the three dimensional growth process and it would seem clear that the factors governing the growth of grain faces should be as well, if not better, described in terms of the processes of random walk than those relating to grains. Accordingly the conclusions reached on the these bases in respect to grain size should also be applicable to grain faces. This suggests that experiments might involve the measurement of the sizes of faces, or rather their physically discernible edges instead of grain diameters. It should be noted that linear dimensions play a dominant role in the foregoing. For compatibility experimental measurements of grain size should be made in a linear fashion.

Comparison of Predictions of Theory with Experiment.

The distribution (9) has been widely criticised (e.g.[Ryum and Hunderi, 1987) as failing to conserve area and volume. We shall now see that this criticism is ill-founded.

Previous considerations have proceeded along the following lines; the total length of a population of N grains is:

$$L = \int \lambda F(\lambda)\, d\lambda = N\lambda_1$$

$$N = \int F(\lambda)\, d\lambda$$

while the total area of the same number of grains is:
and the total volume is:
Substitution for f(λ) from (7) (F and f are of the same form) shows

$$A = \int \lambda^2 F(\lambda)\, d\lambda = NA_0, \qquad (15)$$

$$V = \int \lambda^3 f(\lambda)\, d\lambda.$$

that the length L is independent of time but that A and V are both time dependent. But it must be appreciated that this is exactly how these quantities should behave. To appreciate the arguments involved we can, for simplicity, concentrate on the two dimensional case. It is apparent that the total number of grains laid end to end along a line is N when the length of the line is L and that the total area of these grains is the quantity specified by (18). There is no constraint that this area should be conserved, rather it is required that the area of a cross section of a polycrystal remains invariant during grain growth. Thus, we require that the number of grains in an area L^2 is N^2. Substitution for $F(\lambda)$ from (9) shows, as required, that the quantity:

$$N^2 \int \lambda^2 f(\lambda)\, d\lambda,$$

is invariant with time. Similar conclusions are reached in the case involving three dimensions.

Again, conservation of length is implicit in the stochastic interchanges envisaged in the considerations leading to (9). Frost has investigated similar stochastic interchanges under the several assumptions that area and volume are conserved. He then finds the distributions:

for two dimensions and in the case of three:

Effectively these distributions differ only by numerical

$$A(\lambda) = \lambda \frac{e^{-\frac{\lambda^2}{4_1 \lambda t}}}{A_1 t^2} \qquad (16)$$

$$V(\lambda) = \lambda \frac{e^{-\lambda^2/4\lambda_2 t}}{A_2 t^{5/2}}. \qquad (17)$$

constants. They ((9), (16) and (17) are each found to conserve one and only one, of the variables length , area and volume when subjected to the analysis required for each particular case.

Recent computer simulation studies have concentrated considerable attention on the question of the form of the distribution of grain size and in particular on whether it is better described by some lognormal:

$$g(\lambda) = D \frac{e^{\frac{-(\ln \lambda/\lambda_0)^2}{2\sigma^2}}}{\lambda}. \qquad (18)$$

or by Louat's form (9). Here, D,λ_0 and σ are disposable constants. It is difficult to resolve this question lacking a precise definition of the meaning of grain size and because the result obtained is sensitive to the method of measurement. In two dimensions the alternative measures are :(a) linear intercepts; (b) square roots of areas and (c) mean caliper diameter. In three dimensional simulations the easiest measurement is (d), the cube root of volume. Anderson et al. [loc. cit. 1989] used methods (a) and (b) for two dimensions and (d) for three. From these measurements and experiment (10), the distribution most in accord with (9) was that found experimentally (Hu, loc. cit.) using method (c). Of all four, this is also the method which seems to be best

able to give a good approximation to a linear measure. None of the methods (a), (b) and (d) can be expected to approximate to a linear measure . Thus, bearing in mind that the traversing line of the linear-intercept method is the representation of a line in a three dimensional agglomeration of grains, it is clear that the probability of an intersection at a radius, r, from a grain centre increases linearly with r. It is then easily seen that near-tangential, and hence short, crossings, of grains by the traversing line are relatively frequent and that a consequence the use of linear intercepts will give a distribution that exaggerates the population of small grains. Again, because grain geometry varies with size the appropriate roots of area and volume do not represent linear measures of grain size. However, such invariance is approached symbatically with increasing grain size. Consistently, the distributions found in these three ways differ one from the other at small grains sizes but are nearly coincident with each other and with Louat's form (11) at the larger sizes. Specifically, there is a progressive decrease in relative population density with decreasing grain size as the quantity measured changed successively from linear intercept, to area, to volume. Such trends are readily related to departures from linear measure. For example, for the case where the measurements are of volume (V) we have :

$$\lambda = V^{1/3} / F_0(V) \equiv V^{1/3}/G(\lambda)$$

where $F_0(V)$ is determined only to the extent that,

$$F_0(\infty) = 1, \; F_0'(V) < 0.$$

The length, $V^{1/3}$, exceeds that which would be found by a linear

measure by an amount which is largest at the smallest grain sizes.

Notwithstanding these conclusions one hastens to emphasise that as previously stated "grain-size" is, at present, an ill-defined quantity so that the search for perfection of agreement between theory and experiment is inappropriate now.

A special feature of the transform which invokes spheres is that it can with ease be employed analytically. In this regard it has been reported, and seems widely accepted, that both the lognormal and Louat functions are invariant under its use. As is shown below this is not true.

For invariance, the function involved must be its own transform, so we require, for a density of spheres, ρ, that, (c.f. A(1))

$$\rho \int_0^{\lambda} f(x) \frac{dx}{(\lambda^2 - x^2)^{1/2}} = \frac{f(\lambda)}{\lambda}. \qquad (19)$$

This an integral equation of Abelian type and is readily inverted to give:

$$f(\lambda) = \frac{-2\rho}{\pi} \frac{d}{d\lambda} \int \frac{f(x)\, dx}{(x^2 - \lambda^2)^{1/2}}. \qquad (20)$$

Combining (19) and (20) we have the differential equation:

$$f(\lambda) = \frac{-2\rho}{\pi} \frac{d(f(\lambda)/\lambda)}{d\lambda}.$$

The solution of this equation is necessarily unique and given by functions conforming to the form of (2). We conclude that a lognormal function can be, at most, approximately invariant under the said transformation and then, only when its defining parameters

are such that it approximates Louat's form.

CONCLUSIONS:

The various predictions of the theory of normal grain growth based on the concept of random walk in grain size space are in accord with experiment and computer simulation. These predictions include:

(1) The shape of the grain size distribution function; it being allowed that relatively minor adjustments to the current prediction are necessary to take account of the expected variation in the probability of growth and shrinkage steps with grain size. The effects of non-linearity in measurments and definition of grain size should be similarly small.

(2) A rate of growth, $\lambda_0 \propto t^{1/(m+1)}$, where the factor, m, relates to the pressure dependence of grain boundary velocity, namely: $v = M P^m$. The normally quoted, $t^{1/2}$ behaviour is predicted only for the normal case of newtonian viscosity in which $m = 1$.

(3) The independence of the form of the distribution function on m.

(4) The conformity of the distribution function with the requirement to conserve as required, any one, but not simultaneously more than one, of the trio: length, area and volume.

(5) The equal applicability of the analysis to two and three dimensional grain growth.

(6) The associated invariance of the distribution in two and three dimensions under the customary transform based on the spherical grain approximation.

(7) The lognormal form of the distribution function for grain size

shape.

(8) The observations:

(a) that the mean rate of growth of grains with more than five sides is that of the mean rate of growth of all grains, but in conformity with the concept of random walk individual grains of this class follow random paths involving frequent changes in the directions of growth;

and (b) that in the case of small grains, in general, those with five or fewer sides, the mean rate of growth is less than that of the mean of all grains and progressively decreases as the number of sides decreases.

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Appendix A.

We introduce the operator notation:

$$D_x \equiv \frac{\partial}{\partial x}; \quad I_x \equiv \int_0^x dx$$

and proceed to solve the equation:

Integrating with regard to x i.e. multiplying each term by I_x from the left, we have:

$$\frac{\partial c}{\partial t} - \beta \frac{\partial (c/x)}{\partial x} - \frac{\partial^2 c}{\partial x^2}$$

$$= (D_t - \beta D_x (\frac{1}{x}) - D_x^2) C = 0$$

$$(I_x D_t - \frac{\beta}{x} - D_x) C = f(t)$$

where f(t) is an arbitrary function of the time.

Then multiplying by x^β from the left we have:

$$(x^\beta I_x D_t - \beta x^{\beta-1} - x^\beta D_x) C = (x^\beta I_x D_t - D_x x^\beta) C$$

$$= x^\beta f(t) .$$

Integrating for the second time in the variable, x, we have:

$$(I_x x^\beta I_x D_t - x^\beta) c = \frac{x^{\beta+1}}{\beta+1} f(t) + g(t)$$

so that:

$$(x^{-\beta} I_x x^\beta I_x D_t - 1) C = \frac{x f(t)}{\beta+1} + \frac{g(t)}{x^\beta} .$$

Thus, as required we have two solutions:

$$C_1 = \frac{x f(t)}{1 - x^{-\beta} I_x x^\beta I_x D_t} ;$$

$$C_2 = \frac{x^{-\beta} g(t)}{1 - x^{-\beta} I_x x^\beta I_x D_t} .$$

Here, f(t) and g(t) are arbitrary functions.

We then proceed on the basis that the right hand side can be expanded in infinite series, e.g.:

We require that C = 0 at x = 0 for all t so that the solution, C_2 is not relevant. Again, towards the identification of f(t), we

$$C_1 = xf(t) + x^{-\beta} I_x\, x^{\beta} I_x f'(t) + \ldots\ldots + \ldots$$

$$= x(ft) + \frac{x^3 f'(t)}{2(3+\beta)} \ldots + .$$

note that to accord with the case where $\beta = 0$, we must take:

$$f(t) = t^{-3/2}$$

and then find:

$$C = \frac{x}{t^{3/2}}\left(1 - \frac{1}{2}\cdot\frac{3}{2}\cdot\frac{1}{(3+\beta)}\cdot\frac{x^2}{t} + \frac{1}{2}\cdot\frac{3}{2}\cdot\frac{5}{2}\cdot\frac{1}{3+\beta}\cdot\frac{1}{5+\beta}\left(\frac{x^2}{t}\right)^2 + \ldots + \ldots\right).$$

Appendix; B.

Inter-dimensional Transformation.

We suppose that grains in three dimensions are spherical with their centres dispersed at random and, consistently, that in two dimensions they appear to be circular. On this basis, we observe that a plane of section will intersect a sphere if it passes within a radius distance, d, of its centre. It will make this intersection in a circle of radius, $a \leq d$.

Now, the number of spheres with centres lying in strips distant between d and d+δd from the plane of section is,

$$2c\delta d$$

per unit area, where c is the number of spheres per unit volume. Then, let $F(r)\delta r$ be the fraction of these with radii between r and r+δr. Such spheres intersect the plane in circles with radii in the ranges specified by:

$$a = \sqrt{(r^2-d^2)}, \qquad a+\delta a = \sqrt{(r^2-d^2+2r\delta r)}$$

so that,

$$\delta a = r\ \delta r/a.$$

The number of circles, radius between a and a +δa from strips lying at distances between d and d+δd from the section plane is:

$$2c\delta d\ F(r)\ dr = \frac{2c\ \delta d\ F(r)\ a\ \delta a}{r} = \frac{G(a)\ \delta a}{a}.$$

and the number of circles of radius between a and a + δa from all strips is:

$$2c \int_0^a \frac{F(r)\ r\ dr}{\sqrt{(a^2-r^2)}}\ \delta a = \frac{G(a)\ \delta a}{a}. \qquad (B.1)$$

It easily verified by substituting for F(r) from (12) in (B.1) and writing, r = a cosh θ, that the functions G and F differ only by a numerical constant.

Again, (B.1) is an Abelian integral equation and is easily inverted to give:

$$F(r) = -\frac{2}{\pi}\frac{d}{dr}\int_0^r \frac{G(a)\,da}{\sqrt{(r^2-a^2)}}.$$